A closed loop process for recycling spent lithium ion batteries

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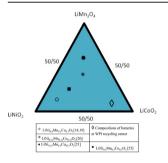
HIGHLIGHTS

- Recovery of materials from spent Lithium ion batteries via a low temperature hydrometallurgical approach.
- The recovery efficiencies for materials in the batteries are determined.
- The impurities are removed so that cathode materials can be recovered as new cathode materials.
- Economics of the process are analyzed.

GRAPHICAL ABSTRACT

ABSTRACT

As lithium ion (Li-ion) batteries continue to increase their market share, recycling Li-ion batteries will become mandatory due to limited resources. We have previously demonstrated a new low temperature methodology to separate and synthesize cathode materials from mixed cathode materials. In this study we take used Li-ion batteries from a recycling source and recover active cathode materials, copper, steel, etc. To accomplish this the batteries are shredded and processed to separate the steel, copper and cathode materials; the cathode materials are then leached into solution; the concentrations of nickel, manganese and cobalt ions are adjusted so $Ni_xMn_yCo_z(OH)_2$ is precipitated. The precipitated product can then be reacted with lithium carbonate to form $LiNi_xMn_yCo_zO_2$. The results show that the developed recycling process is practical with high recovery efficiencies ($\sim$90%), and 1 ton of Li-ion batteries has the potential to generate $5013 profit margin based on materials balance.

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1. Introduction

Due to their high energy density, long lifespan and light weight, lithium ion (Li-ion) batteries accounted for $11.8 billion dollars in sales in 2012, that makes up 60% of total portable battery sales and 37% of total battery sales [1]. The same factors also make them the best candidate for use in hybrid electric vehicles (HEVs) and electric vehicles (EVs). Currently many Li-ion batteries are already used in HEVs and EVs; total all time worldwide HEV sales were 1.5 billion as of 2011 billion and are expected to reach nearly 3.5 billion by 2015 [2]. One reason for the increased use of Li-ion batteries in the vehicle market is the ever-stricter CO_2 emission standards automobile manufacturers must meet [3].

The working principle of the Li-ion battery is that of a galvanic cell. When charging, Li-ions transfer from the cathode to the anode through the electrolyte, and electrons are transferred from the cathode to the anode via the external circuit. When discharging, Li ions transfer from the anode to the cathode through the electrolyte, and electrons are transferred from the anode to the cathode through the external circuit. With every cycle of charging and discharging, Li ions traverse back and forth between anode and cathode. There are 2 primary failure mechanisms in Li-ion batteries (1) secondary reactions, and (2) dendrite growth [4]. Studies on Li-ion battery cycling in HEVs predict Li-ion batteries can run for

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Table 1
Li-ion battery components by weight percent [9].

Battery component	Wt%
Casing	25
Cathode material	25
Anode material	14
Electrolyte	10
Copper electrolyte foil	8
Aluminium electrolyte foil	5
Separator	4
Other	6

between 1700–5300 cycles depending on operating conditions, which puts the operating lifetime of the battery at 4.5–14.5 years [5,6].

Li-ion batteries are made of an anode, a cathode, current collectors, a separator, liquid electrolyte, container and sealing parts. Table 1 shows the contribution that each component makes to the total battery weight. The anode is made of graphite, carbon and polyvinylidene fluoride (PVDF) binder; the anode current collector is copper. The electrolyte is lithium hexaflourophospate ($LiPF_6$) with an organic solvent commonly ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) or their mixture. The separator is made of polypropylene (PP) or polyethylene (PE). The cathode is made of carbon, the PVDF binder and a lithium compound and the cathode current collector is aluminium foil.

The first generation Li-ion batteries used $LiCoO_2$ as the cathode and recycling Li-ion batteries with $LiCoO_2$ cathode materials has been widely studied [7]. Today however a wide variety of lithium compounds are used as cathode materials mostly commonly $LiCoO_2$, $LiMn_2O_4$, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, and $LiFePO_4$. The most expensive part of the battery is the cathode materials and the composition of the cathode can vary greatly as new technologies are developed to produce low-cost and high energy density Li-ion batteries. Fig. 1 shows the value of each component in 1 ton of Li-ion batteries. The amount of cathode materials in 1 ton of batteries was calculated using the forecasted 2012 Li-ion battery cathode chemistry makeup [1], and the value of the cathode materials was obtained from Gaines et al. [8]. The amount of each battery material in 1 ton of batteries was calculated using the wt% provided by Maschler et al. [9]. From the figure, the intrinsic material value for 1 ton of Li-ion batteries is $7708. The greatest value is from cathode
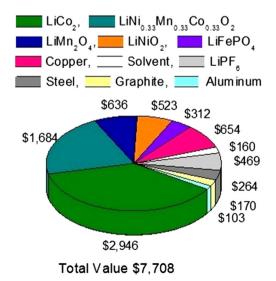
materials including $LiCoO_2$ ($2946), $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ ($1684), $LiMn_2O_4$ ($636), $LNiO_2$ ($523) and $LiFePO_4$ ($312), and Cu ($654), and steel ($212). These materials account for ~90% of the total intrinsic material value, which will be recycled in our proposed process. Current processes mainly recycle Co and Ni as pure metals and therefore the potential value is significantly lower than our process.

As the chemistry of cathode materials changes, it is important for recyclers to be aware that the target recycling stream of incoming batteries is going to be at least 3–4 years old. Currently, Li-ion battery recycling efforts have focused on recovering cobalt from $LiCoO_2$ cathode material. $LiCoO_2$ is the predominate material in the recycling stream today [10–12]. In a recent review paper by Xu et al. [7], the existing recycling methods considered only $LiCoO_2$ as the cathode material. $LiCoO_2$ is not the only cathode material used in the commercial world, for example currently $LiCoO_2$ is only used as the cathode material in ~37.2% of the Li-ion batteries, other battery chemistries are $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ is used in ~29.0%, $LiMn_2O_4$ is used in ~21.4%, $LiNiO_2$ is used in 7.2% and $LiFePO_4$ is used in ~5.2% [1]. New battery chemistries with less Co and Ni are being used in order to lower battery prices. For example, $LiMn_2O_4$ is used as the cathode material for GM Volt batteries, and $LiFePO_4$ is used as the cathode material in A123 batteries. Thus recovering all cathode materials regardless of battery composition is critical because these batteries will be entering the recycling stream soon and present technologies are not in place to handle them. Some work has been carried that focuses on recycling of Li-ion batteries with varying cathode chemistries [13,14], however they are complex and commercially not feasible since those methods are trying to separate every element/material in the cathode.

Industrially, companies such as Umicore, Recupyl Battery Solutions, and Toxco do recycle Li-ion batteries. Umicore uses an ultrahigh temperature smelting technology [15,16] and does offer a closed loop solution for high value metals such as Co and Ni. Less valuable metals such as Mn, Fe, Li, Al are 'downcycled', meaning that they are not recovered and reused in battery applications. It is believed that Toxco focuses on Li-ion batteries with $LiCoO_2$ chemistry [17].

The main issue with recycling Li-ion batteries with different cathode chemistries is that cobalt, manganese, and nickel are hard to separate from one another, without using expensive organic reagents for solvent extraction [13,14]. The proposed process addresses this issue by offering a closed loop recycling process where new cathode materials can be made from spent lithium ion batteries. We have previously shown that unused Li-ion cathode powders consisting of $LiFePO_4$, $LiCoO_2$, $LiMnO_2$, and $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ can be recycled to recover $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ and $Fe(OH)_3$ by precipitating $Ni_{0.33}Mn_{0.33}Co_{0.33}(OH)_2$ and reacting the precipitate with lithium carbonate, which is produced by reacting the remaining lithium hydroxide with sodium carbonate [18]. In this study we recover $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, copper and steel from spent Li-ion batteries obtained from Worcester Polytechnic Institute (WPI) recycling center. The batteries used in this experiment are primarily composed of $LiCoO_2$ cathode chemistry and in a second experiment, cathode materials are recovered from spent Li-ion batteries with $LiMn_2O_4$, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ and $LiFePO_4$ powders added to the shredded used batteries. In both cases the batteries are discharged, then shredded. The steel casing is removed from the shredded material by magnetic separation. The cathode materials are separated from the aluminium current collectors by dissolving the aluminium in NaOH. The powders are then separated from the rest of the material by sieving. The copper current collectors are then separated from the remaining material, mainly plastic, by density separation. The cathode materials are then leached into solution and the $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ product is

Fig. 1. Cost breakdown of each component in 1 ton of Li-ion batteries [1,8,9]. Total value of all components is $7708.
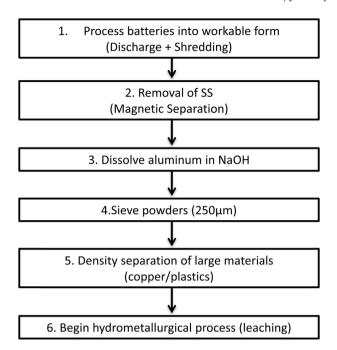
Fig. 2. Procedure for processing spent Li-ion batteries to recover steel and copper, as well as separating cathode powders to begin hydrometallurgical procedure.

recovered via our hydrometallurgical process, see Fig. 2. One major advantage of this process is that concentrations of nickel, manganese and cobalt in the recovered cathode material can be specifically tailored. A wide variety of $LiNi_xMn_yCo_zO_2$ compounds have been used in Li-ion batteries [19–24]. Fig. 3 shows the compositions of several compound $LiNi_xMn_yCo_zO_2$ compounds, all of which can be made by this process by adding the metal sulphates to the leaching liquor to the desired compositions.

2. Experimental

2.1. Testing Cu impurity removal

When the concentration of Ni in solution is high, it is possible to remove Ni ions before the concentration of the Cu impurity reaches
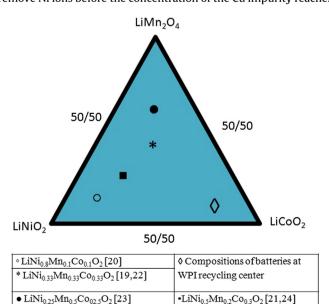
the desired 10^{-5} M level. Furthermore, previously researchers have proposed that Co ions are removed with $Cu(OH)_2$ at to the formation of a Cu–Co complex [25]. However, these experiments were conducted with very concentrated basic solutions such that the change in volume during pH adjustment was negligible. In order to test this theory with a less concentrated base, two experiments were conducted, one with copper and one without. In the experiment with copper, 5.5 g $NiSO_4·7H_2O$, 5.0 g $CoSO_4·6H_2O$, 4.23 g $MnSO_4·H_2O$ and 0.1 g copper foil were added to 50 ml 4 M H_2SO_4 with 10 wt% H_2O_2. In the second experiment, the same masses of nickel, cobalt and manganese sulfate without copper foil were put into the solution containing 50 ml 4 M H_2SO_4 with 10 wt% H_2O_2. After allowing the solutions to react for 2 h the solutions were diluted to 100 ml with DI water in a 100 ml volumetric flask. The concentrations of Co, Ni, Mn and Cu present in solution were measured with atomic adsorption spectroscopy (AAS) (Perkin–Elmer AA Analyst 300). The pH was then increased to 6.5 by adding 2 M NaOH. Once the pH reached 6.5, the solutions were allowed to stir for 4 h, then the solutions were diluted to 250 ml with DI water in a 250 ml volumetric flask. The concentrations of Co, Ni, Mn and Cu present in solution were measured with AAS.

2.2. Processing spent Li-ion batteries

Before Li-ion batteries can go through the hydrometallurgical route to recover the cathode materials, the spent Li-ion batteries must be processed, so that the lithium compounds can be leached into solution.

All Li-ion batteries collected were used in cell phones or laptops. For the laptop batteries, the plastic casing that holds the 18650 cells was removed by hand. The cell phone batteries were left as is. The batteries were then processed so they can be recycled. Fig. 2 shows the procedure for processing Li-ion batteries into a form that will allow the cathode materials to be leached into solution, as well as recovering the copper and steel.

Step 1: Before Li-ion batteries can be safely shredded, they must be discharged due to the remaining capacity in batteries and the possibility of a short circuit in the presence of the flammable electrolyte [26]. 18 18650 cells from laptop batteries and 6 cell phone batteries were discharged in a stainless steel container with stainless steel chips for 4 h, this is similar to the procedure proposed by Nan et al. [12]. After discharge the voltages were measured with a voltmeter and all were below 2.0 V.
Step 2: After discharging, the batteries were shredded in a Schutte Buffalo Hammer Mill (Laboratory Scale, Model-6-H). The hammer mill had contained a screen with ¼″ holes and was run at 2,000 rpm. After shredding, random 20 g samples were used for the remaining experiments.
Step 3: The steel casings in the 20 g sample were removed with a rare earth. The magnet was passed 1″ above a monolayer of the shredded batteries until no more pieces were attracted to the magnet.
Step 4: The remaining material was exposed to 75 ml of 2 M NaOH to dissolve the anode current collectors (aluminium) according to Eq. (1). The solution was given 2 h to react.

$$2Al + 2NaOH = 2NaAl(OH)_4 + 3H_2(g) \qquad (1)$$

Step 5: The material was sieved with a 250 μm screen after drying at 60 °C. The sub 250 μm fraction was composed primarily of cathode powders, carbon and a small amount of copper.

○ $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ [20]	◇ Compositions of batteries at
* $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ [19,22]	WPI recycling center
● $LiNi_{0.25}Mn_{0.5}Co_{0.25}O_2$ [23]	▪ $LiNi_{0.5}Mn_{0.2}Co_{0.3}O_2$ [21,24]

Fig. 3. Composition of common Li-ion nickel, manganese, cobalt cathode materials.

Step 6: The fraction with larger than 250 μm consists primarily of copper and the plastic separator. The copper, density 8.96 g cm^{-3}, and plastic (polyethylene), density ~0.9 g cm^{-3} were separated by heavy media. The material was put into a solution of diiodomethane (Alfa Aesar) density 3.3 g cm^{-3} and the material was allowed to settle for 30 min. After 30 min the material on the surface of the diiodomethane was skimmed off and separated from the sunken material.

2.3. Processing spent Li-ion batteries with added cathode powders

All steps follow the procedure for the previous section. Except in step 5, 2.07 g of LiMn$_2$O$_4$, 2.73 g of LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ and 0.49 g LiFePO$_4$ powders were added to the sub 250 μm fraction. These masses were chosen to make a composition of cathode powders present representative of the 2012 battery market. Based on previous experiments 75% of the mass of the sub 250 μm fraction was assumed to be LiCoO$_2$. Therefore based on the assumed mass of LiCoO$_2$, the masses of LiMn$_2$O$_4$, LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ and LiFePO$_4$ powders were calculated.

2.4. Hydrometallurgical recovery of cathode materials

The sub 250 μm fraction from step 5 above and the light material from step 6 were taken through the hydrometallurgical process. The plastics were included in the leaching solution because it was observed that some cathode material had attached to the plastic separator after shredding. Since the cathode powders leach into solution and the plastics do not, they were easily separated by filtration in the first step of the hydrometallurgical process.

Step 1: The powders and plastics were leached into solution using 60 ml of 4 M sulphuric acid and 10 ml of 50wt% hydrogen peroxide at 65–70 °C. After allowing the solutions to react for 2 h, the solutions were diluted to 100 ml with DI water in a 100 ml volumetric flask. The concentrations of Co, Ni, Mn, Li, Al, Fe and Cu present in solution were measured with AAS. Carbon and residual LiFeO$_4$ did not dissolve into solution and were filtered out.
Step 2: The pH of the solution was increased to 6.47 by adding 2 M NaOH. The precipitate was filtered from solution, washed and dried. AAS was performed on the remaining solution. The rational for increasing the pH to 6.45–6.5 was to remove all the Fe, Al, and Cu impurities. Once the pH reached 6.45–6.5 the solutions were allowed to stir for 4 h, then the solutions were diluted to 250 ml with DI water in a 250 ml volumetric flask.

Because Fe, Al and Cu are present in Li-ion batteries and they leach into solution when exposed to 4 M H$_2$SO$_4$ with H$_2$O$_2$, they are therefore common impurities in the recovered cathode materials, if steps are not taken to remove them from solution. Shown in Table 2 is the pH versus concentration in solution of the impurities

Table 2
pH versus concentration of desired elements.

Material	pH at 1 M	pH at 10^{-5} M
Fe(OH)$_3$	1.14	2.81
Al(OH)$_3$	2.82	4.49
Cu(OH)$_2$	4.15	6.85
Ni(OH)$_2$	6.37	8.87
Co(OH)$_2$	6.9	9.38
Mn(OH)$_2$	7.65	10.15

Fe(OH)$_3$, Al(OH)$_3$ and Cu(OH)$_2$ for ideal solutions; Ni(OH)$_2$, Co(OH)$_2$ and Mn(OH)$_2$ are included to determine if it is possible to precipitate them out before the impurities are removed and reduce the recovery efficiency and the reactions shown below. This table ignores common ion effects. The reactions for precipitation of nickel, manganese and cobalt hydroxide are shown in Eqs. (2)–(4). If one of these reactions occur before Ni$_x$Mn$_y$Co$_z$(OH)$_2$ is precipitated or before Fe(OH)$_3$, AL(OH)$_3$ or Cu(OH)$_2$ is precipitated, then recycling efficiency will be reduced. The solubility constant for Ni$_x$Mn$_y$Co$_z$(OH)$_2$ is unknown at this time.

$$Ni^{2+} + 2NaOH = Ni(OH)_2 + 2Na^+ \quad (2)$$

$$Co^{2+} + 2NaOH = Co(OH)_2 + 2Na^+ \quad (3)$$

$$Mn^{2+} + 2NaOH = Mn(OH)_2 + 2Na^+ \quad (4)$$

Step 3: The concentration of Co, Ni, Mn, Li, Al, Fe and Cu in solution was measured with AAS. Then MnSO$_4$ and NiSO$_4$ were added to adjust the ratio of Co, Ni, and Mn to 1:1:1. This ratio can be changed based on the target materials, which is one of the biggest advantages of our process.
Step 4: The pH was increased to 11 to precipitate out Ni$_{0.33}$Mn$_{0.33}$Co$_{0.33}$(OH)$_2$. It was shown previously that at pH 11 the concentrations of CoSO$_4$, NiSO$_4$ and MnSO$_4$ are less than 10^{-7} M [18].

2.5. Synthesis of LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$

The precipitated Ni$_{0.33}$Mn$_{0.33}$Co$_{0.33}$(OH)$_2$ was mixed with Li$_2$CO$_3$ in molar ratio 1:1.1 and then ground in the mortar. The precursor was subjected to ball-milling for 48 h and pressed into pellets (Pressure = 15000lbs, 12.96 mm diameter). The pellets were then sintered at 900 °C for 15 h in air, and the temperature was increased at a rate of 9 °Cmin^{-1} from room temperature. The reaction product was ground into powder using a mortar and pestle.

2.6. Characterization

The crystal structure of the Ni$_{0.33}$Mn$_{0.33}$Co$_{0.33}$(OH)$_2$/Ni$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O(OH) precipitate and LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ was characterized using an X-ray diffractometer (Bruker D8 Focus; S/N 203207 with copper Kα radiation, Cu target: S/N 07/03-1120). X-ray scintillation detector SD 650 Nal (TI) was used. The concentration of metal ions in solution was tested by AAS. The scanning electron microscopy (SEM) images were obtained with a JEOL JSM-7000F electron microscope. The pH of the solution was tested with a Milwaukee MW102 pH meter.

3. Results and discussion

3.1. Testing Cu impurity removal

The concentrations of Co, Ni, Mn and Cu after adding their sulphates to water were measured as a function of pH shown in Table 3. The results show that even when copper is present in the initial solution there is at least 96% of Ni, Co and Mn remaining in solution at pH 6.5, while only 14.5 ppm copper remained in solution. Thus this is a suitable method for recovering Co, Ni and Mn from spent Li-ion batteries while keeping the copper impurity concentration low. Based on the solubility constant for copper shown in the appendix the concentration of copper in solution should be on the order of 1 ppm. However, this represents a

Table 3
Efficiency of recovery for Co, Ni, and Mn with and without Cu.

	Concentration at pH > 1 (ppm)	Total mass at pH > 1 (g)	Concentration at pH > 6.5 (ppm)	Total mass at pH > 6.5 (g)	Difference	Efficiency (% of original)
Experiment with Cu						
Co	12320	1.23	4739	1.18	0.05	96
Ni	13540	1.35	5329	1.33	0.02	99
Mn	12260	1.22	4697	1.17	0.05	96
Cu	989.5	0.099	14.54	3.63×10^{-3}	0.095	3.6
Experiment without Cu						
Co	12230	1.22	4881	1.22	0	100
Ni	13540	1.35	5528	1.38	+0.03	102
Mn	12280	1.23	4892	1.22	0.01	99
Cu	ND		ND		NA	

simplistic view of the problem, as there are many ions in solution and common ion effects would need to be taken into consideration.

3.2. Processing 20 g of Li-ion batteries

3.2.1. Shredding

Shredding is an important step in processing the batteries because the batteries must be processed into a workable form. By using a hammer mill the batteries were processed into a workable size less than ¼″ dimensions, Fig. 4.

3.2.2. Magnetic removal

A rare earth magnet was passed over the material in Fig. 4. This removed 4.77 g of material, and the material was primarily steel pieces on the order of 3 mm in diameter. These steel pieces contained non-ferrous attachments which were removed by hand and weighed to be 0.091 g. The removed material is shown in Fig. 5. Of this 0.085 g was found to be cathode materials, this represents 1.7% of the total theoretical cathode materials present in 20 g of shredded batteries.

3.2.3. Aluminium dissolution

2 M NaOH solution was analyzed with AAS to determine if any cathode materials were removed during the exposure to the caustic solution. Aluminium was measured to be 9128 ppm, Fe, Cu, Co, Mn, and Ni were all below the detection limit of AAS. The mass of material remaining after reactions with the 2 M NaOH was 13.58 g.

3.2.4. Sieving

The material was sieved in a 12 in diameter 250 μm screen. The mass of the sub 250 μm fraction was 3.79 g. The fraction with mass greater than 250 μm weighed 4.62 g.

3.2.5. Density separation

The heavy fraction weighed 1.62 g and the light fraction weighed 3.01 g. The sunk materials are shown in Fig. 5. The sunk fraction was leached into H_2SO_4 and H_2O_2, and the amount of cathode materials were measured. The cathode materials weighed 0.3 g which represents 6% of the total theoretical cathode materials present in 20 g of shredded batteries.

3.2.6. Leaching recovered powders

The composition of the leached solution was measured with AAS before and after increasing the pH to 6.47, Table 4. After leaching, 4.58 g $NiSO_4 \cdot 7H_2O$ and 3.87 g $MnSO_4 \cdot H_2O$ were added to the solution so that the Co:Ni:Mn atomic ratio was 1:1:1.

The product was precipitated at pH 11. The mass of the recovered product was 9.5 g after drying in air at 75 °C for 24 h. After crushing the product with a mortar and pestle, a 1.75 g sample was removed from the product and leached into the sulphuric acid/
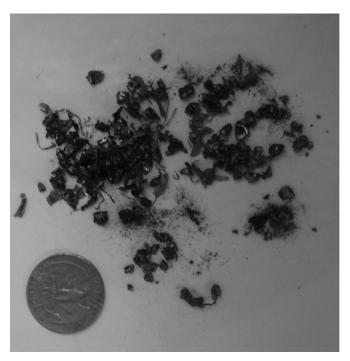

Fig. 4. Hammer milled Li-ion batteries with ¼″ screen spacing (step 1).

Fig. 5. Material separated from hammer milled batteries by rare earth magnet (step 2).

Table 4
Impurity levels (ppm) in solution.

	Cu	Fe	Al	Mn	Co	Ni
pH < 1	2863	471.4	2986	608.3	16952	1160
Grams total	0.286	0.0471	0.2986	0.0608	1.69	0.116
Adjusted total	0.2574	0.0424	0.268	0.0547	1.526	0.104
Ph = 6.47	ND	ND	ND	208.4	5633	296.8
Total grams	ND			0.0528	1.408	0.074
Recovery efficiency				97%	92%	71%

hydrogen peroxide solution. The composition of the product solution after leaching is shown in Table 5. Additionally, Table 5 shows the impurity concentration of Fe, Al and Cu to be less than 50 ppm. It is believed that Li-ion battery cathode materials need impurity concentrations less than 100 ppm. The cathode materials are made by solid state reaction of $Ni_{0.33}Mn_{0.33}Co_{0.33}(OH)_2$ with Li_2CO_3, if both components have impurity levels less than 50 ppm then the $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ product will have impurity levels less than 100 ppm. Therefore, increasing the pH to 6.47 is sufficient to remove the impurities in order to produce precursors for Li-ion batteries.

The XRD spectrum of the recovered product is shown in Fig. 6. The product is a mixture of $Ni_{0.33}Mn_{0.33}Co_{0.33}(OH)_2$ and $Ni_{0.33}Mn_{0.33}Co_{0.33}O(OH)$ phases. To precipitate the pure $Ni_{0.33}Mn_{0.33}Co_{0.33}(OH)_2$ phase, the precipitation process needs to be carried out under nitrogen [27].

3.2.6.1. Final recovery efficiency. The recovery efficiency of all Co, Ni and Mn in solution was 94%, 96% and 91% respectively when accounting for the initial concentrations of Co, Mn and Ni and the added metal sulphates. The recovery efficiency is greater than 90% which is sufficient for recycling Li-ion batteries. The atomic ratio of the Mn:Co:Ni in the $Ni_{0.33}Mn_{0.33}Co_{0.33}O(OH)$ and $Ni_{0.33}Mn_{0.33}Co_{0.33}(OH)_2$ recovered product is 1.000:1.005:1.069.

3.3. Processing 20 g of Li-ion batteries with added cathode powders

20 g of shredded Li-ion batteries were processed using the procedure previously described. The pH was increased to 6.47 to remove the impurities, over 99% of the impurities where removed, Table 6. At pH 6.47 over 90% of the manganese and nickel ions remained in solution and over 80% of the cobalt ions remained in solution. The decrease in the efficiency of cobalt recovery is believed to be due to the increase in cobalt concentration from the added $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ powders. 5.59 g of $NiSO_4 \cdot 6H_2O$, 1.12 g $CoSO_4 \cdot 5H_2O$ and 0.53 g $MnSO_4 H_2O$ were added so the precipitated product would have a Ni:Mn:Co atomic ratio of 1:1:1. The pH was then increased to 11 with 2 M NaOH to precipitate out the $Ni_{0.33}Mn_{0.33}C_{0.33}(OH)_2$ product.

3.3.1. Final recovery efficiency

11.6 g of product was recovered by precipitation, and 1.58 g of the product after drying, was leached into 20 ml of 4 M H_2SO_4 and
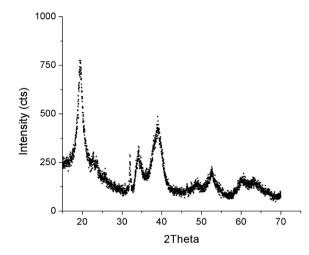

Fig. 6. XRD of $Ni_{0.33}Mn_{0.33}Co_{0.33}O(OH)$ product precipitated out of solution at pH 11.

9 ml of 50wt% H_2O_2. 1.95 g of cobalt was recovered; 1.71 g of manganese and 1.83 g of nickel were also recovered (Table 7). The atomic ratio of recovered Mn, Ni, and Co was 1:1.02:1.08, respectively (Table 7). The Fe, Al and Cu were all under 50 ppm. The efficiency of recovery for all Co, Mn and Ni ions added from batteries/cathode powders and sulphate solutions was 86%, 98% and 95% respectively. The total recovery efficiency was greater than 85% for all of the target metals.

3.4. Characterization of $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$

The XRD of the synthesized $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ prepared from the recovered $Ni_{0.33}Mn_{0.33}Co_{0.33}(OH)_2$ is shown in Fig. 7. Lattice parameters of samples were calculated from the d-value of 10 strong diffraction peaks. The sample peaks can be indexed as α-NaFeO₂ structures with a space group of $R\bar{3}$ m. Distinct splitting of (006)/(012) and (018)/(110) peaks indicates that the sample possesses a well-developed layered-structure [28]. No impurity peaks are present in either pattern, which suggests that $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ is of high purity.

The SEM image of the $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ product is shown in Fig. 8. Homogenous particles are well distributed throughout without any agglomeration; particle size ranges from 200 to 300 nm. Uniform particle size and homogenous particles are critical factors for high quality materials. Smaller particle size allows a shorter lithium diffusion length, which in turn provides higher battery performance, which has been demonstrated in the previous results [18].

3.5. Waste management

The process produces minimal waste. The residual basic solution can be neutralized and disposed. The amount of solution generated 3112 L ton^{-1} of Li-ion batteries recycled based on the ratios of acid

Table 5
Composition of hydroxide product.

	Co	Mn	Ni	Fe	Cu	Al	Li
Product (ppm)	2991	2852	3185	0.90	5.2.0	ND	23.00
Product (g)	0.299	0.285	0.319	9.0E-5	5.2E-4		2.3E-3
Total in sample (g)	1.615	1.514	1.72	4.8E-4 (5 ppm)	2.8E-3 (29 ppm)		0.0129

Table 6
Impurity concentration at pH 6.47 for batteries with added cathode powders.

	Cu	Fe	Al	Mn	Co	Ni
pH < 1 (ppm)	4274	2400	3358	15840	23270	7675
Mass (g)	0.427	0.24	0.33	1.58	2.327	0.767
Adjusted total (g)	0.363	0.204	0.281	1.343	1.978	0.652
Ph = 6.47 (ppm)	9.99	3.49	8.4	5395	6591	2381
Mass (g)	2.5e-3	8.73e-4	2.1e-3	1.34	1.648	0.595
Recovery efficiency	0.68%	0.4%	0.7%	100%	83.4%	91.2%

Table 7
Composition of hydroxide products.

	Co	Mn	Ni	Fe	Cu	Al	Li
Product (ppm)	9181	7862	8630	1.3	2.6	1.45	287
Product (g)	0.266	0.227	0.25	3.77E-5	7.54E-5	4.21E-5	8.3E-3
Total in sample (g)	1.954	1.673	1.834	2.39E-5 (24 ppm)	4.77E-5 (47 ppm)	2.66E-5 (27 ppm)	0.061

and base used to battery materials used in this paper. However, since the solution is non-toxic the basic solution can be neutralized and disposed. The amount of acid required to neutralize 3112 L of solution is less than $5 based on our calculation and therefore not included in the economic analysis section that follows.

3.6. Economic analysis

By analyzing the recovery efficiency of each step in the 20 g process (Figs. 1 and 2) we can scale to 1 ton of batteries and adjust the economic analysis from previous research [18]. The amount of cathode materials removed during magnetic separation represents 4.25 kg or 1.7% of 250 kg and 1.5 kg during density separation or
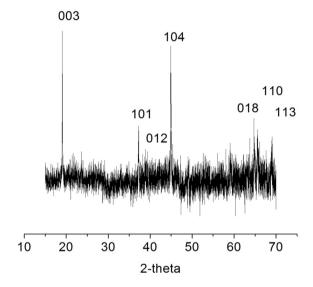

Fig. 7. XRD of LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ is from made from recycled batteries.
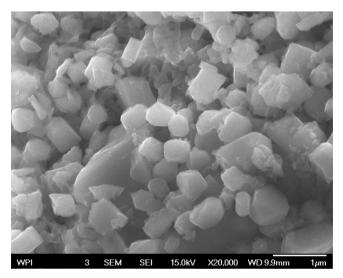

Fig. 8. SEM image of recovered LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$.

0.6% of 250 kg. The efficiency of getting cathode materials from the battery and into solution was measured to be 97.7% based on the amount of cathode material lost during magnetic and density separation (sections 3.2.2 and 3.2.5). The efficiency of hydrometallurgical process is expected to be 90%. Thus the total recovery efficiency of the cathode materials is expected to be 88%. Therefore it is expected that 249.99 kg of steel will be recovered, 62 kg of copper, 220 kg of cathode materials and 121 kg of sodium aluminate based on the masses in 1 ton of Li-ion batteries (Table 1). The value of the recovered products with these efficiencies is expected to be $6432/ton (Table 8), with over 90% of the recovered value coming from the new cathode materials. The chemical cost to recycle the batteries is expected to be $1419/ton shown in Table 9. This results in a profit margin of $5013. It is noted that we only consider the material balance. In the future, we will add the labor cost, equipment cost and energy cost in the economical analysis.

4. Conclusion

We have demonstrated the feasibility of recycling Li-ion batteries regardless of cathode chemistry via a low temperature hydrometallurgical process. The key to this process is the recovery of a specific targeted nickel manganese cobalt hydroxide, and in this research Ni$_{0.33}$Mn$_{0.33}$Co$_{0.33}$(OH)$_2$ was targeted and recovered. The Ni$_{0.33}$Mn$_{0.33}$Co$_{0.33}$(OH)$_2$ was used to produce new cathode LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$, other cathodes maybe produced depending on the target nickel manganese cobalt ratio. The purity of the Ni$_{0.33}$Mn$_{0.33}$Co$_{0.33}$(OH)$_2$ recovered was high, with less than 50 ppm of Al, Cu and Fe impurities. It is important to have high purity so that the performance of the LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ is not compromised. The recovery efficiency of the valuable cathode metals, Ni, Co and Mn, was ~90%. Accounting for and scaling the efficiencies measured by this process, resulted in a margin of $5013/ton between the value of materials recovered and the cost of materials to recycle.

Table 8
Value of recovered materials.

Material	Mass (lbs)	$/lb	Value ($)
Steel	550	0.25	138
Copper	136.4	3.40	464
Sodium aluminate	266	1.32	351
LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$	670	8.8	5899
Total			6432

Table 9
Chemical cost to recycle lithium ion batteries.

Chemical	Mass (lb)	$/lb	Cost
NaOH	584.8	0.16	93
H$_2$SO$_4$	675.4	0.07	46
H$_2$O$_2$ (30 wt%)	235	0.23	53.4
MnSO$_4$*H$_2$O	208.7	0.27	56.4
NiSO$_4$*7H$_2$O	379.7	2.73	1036.7
Li$_2$CO$_3$	251.4	3.63	9,14.18
Total cost			1419.4
Margin			5013

Acknowledgments

References

[1] Lithium-ion Battery Market: Cell & Components, Yano Research Institute, 2011.
[2] B. Scrosati, J. Garche, J. Power Sources 195 (9) (2010) 2419—2430.
[3] M. Armand, J.M. Tarascon, Nature 451 (7179) (2008) 652—657.
[4] J.M. Tarascon, M. Armand, Nature 414 (6861) (2001) 359—367.
[5] S.B. Peterson, J. Apt, J.F. Whitacre, J. Power Sources 195 (8) (2010) 2385—2392.
[6] A. Millner, Modeling lithium ion battery degradation in electric vehicles, in: Innovative Technologies for an Efficient and Reliable Electricity Supply (CIT-RES), 2010 IEEE Conference on, 2010.
[7] J. Xu, et al., J. Power Sources 177 (2) (2008) 512—527.
[8] L. Gaines, A comparison of Li-ion battery recycling options, in: SAE International, SAE International, Detriot, 2012.
[9] T. Georgi-Maschler, et al., J. Power Sources 207 (0) (2012) 173—182.
[10] C.K. Lee, K.-I. Rhee, Hydrometallurgy 68 (1—3) (2003) 5—10.
[11] M. Contestabile, S. Panero, B. Scrosati, J. Power Sources 83 (1—2) (1999) 75—78.
[12] J. Nan, D. Han, X. Zuo, J. Power Sources 152 (0) (2005) 278—284.
[13] R.-C. Wang, Y.-C. Lin, S.-H. Wu, Hydrometallurgy 99 (3—4) (2009) 194—201.
[14] A. Chagnes, B. Pospiech, J. Chem. Technol. Biotechnol. (2013).
[15] D. Cheret, S. Santen, Battery Recycling, 2007. Google Patents.
[16] F. Tedjar, J.-C. Foudraz, Method for the Mixed Recycling of Lithium-Based Anode Batteries and Cells, 2010. Google Patents.
[17] C. Vadenbo, Prospective Environmental Assessment of Lithium Recovery in Battery Recycling, ETH IED-NSSI. ETH Zürich, Zürich, 2009, p. 174.
[18] H. Zou, et al., Green. Chem. 15 (5) (2013) 1183—1191.
[19] L. Wang, et al., J. Solid State Electrochem. 13 (8) (2009) 1157—1164.
[20] M.-H. Kim, et al., J. Power Sources 159 (2) (2006) 1328—1333.
[21] Z. Liu, A. Yu, J.Y. Lee, J. Power Sources 81—82 (0) (1999) 416—419.
[22] J.-M. Kim, H.-T. Chung, Electrochim. Acta 49 (6) (2004) 937—944.
[23] J. Choi, A. Manthiram, J. Power Sources 162 (1) (2006) 667—672.
[24] S.-W. Cho, K.-S. Ryu, Mater. Chem. Phys. 135 (2—3) (2012) 533—540.
[25] T. Suzuki, et al., Sep. Purif. Technol. 98 (0) (2012) 396—401.
[26] T. Tanii, et al., Method for Crushing Cell, 2003. Google Patents.
[27] A. van Bommel, J.R. Dahn, J. Electrochem. Soc. 156 (5) (2009) A362—A365.
[28] J. Liu, et al., J. Power Sources 174 (2) (2007) 701—704.